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DOI:

[10.1021/acs.jpcc.6b05133](https://doi.org/10.1021/acs.jpcc.6b05133)

Document Version

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Citation for published version (APA):

Mansourian, A., Paknejad, S. A., Zayats, A. V., & Mannan, S. H. (2016). Stereoscopic Nanoscale-Precision Growth of Free-Standing Silver Nanorods by Electron Beam. *Journal Of Physical Chemistry C*, 120(36), 20310–20314. <https://doi.org/10.1021/acs.jpcc.6b05133>

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Stereoscopic Nanoscale-Precision Growth of Free-Standing Silver Nanorods by Electron Beam Irradiation

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ABSTRACT: Nanoscale manipulation of atoms is desirable in modern technologies. Atoms in a material are typically manipulated by mechanical contact or thermal and electric effects. The electron beam of a scanning electron microscope is usually used for two-dimensional patterning of a substrate with nanoscale precision. Here we report stereoscopic growth of nanoparticles and nanorods on silver surfaces with nanometric precision under exposure to the electron beam with precise control over their position, size, and orientation. Nanorod length (50–1000 nm) and diameter (30–100 nm) can be independently controlled by adjusting the electron beam characteristics of a scanning electron microscope. Silver nanorods with diameters as small as 30 nm with location accuracy limited only by the resolution of the scanning electron microscope have been fabricated with repeatable orientation and size. Cascaded nanorod structures can be grown directly on other nanorods. The results open up a number of exciting possibilities for three-dimensional, nanoscale-controlled direct fabrication of nanoparticles and nanowires by an electron beam *in situ* using conventional SEM facilities.

Introduction

Controllable fabrication of nanostructures is a cornerstone of modern nanoelectronic, optoelectronic and nanophotonic technologies. Both top-down, as well as, bottom-up approaches for the fabrication of nanostructured devices, have been developed.¹ Electron Beam Lithography (EBL)² and Focused-Ion-Beam (FIB) milling³ are two sophisticated fabrication techniques that require specialized equipment and are still primarily limited to two-dimensional objects while full control over three-dimensional positioning and orientation of individual nanostructures on planar and, especially, curved surfaces is still in its infancy.

Here we demonstrate a stereoscopic growth of Ag nanorods on a surface of Ag nanorods, resulting in a 3D nanostructure, in vacuum conditions with dimensions, orientation and position controlled by the electron beam parameters of a scanning electron microscope (SEM). We present results of nanorod on nanorod formation with precise control over diameter (30—70 nm) and length (50—1000 nm) achieved by adjusting the exposure time and nanorod positioning better than 5 nm limited by the electron-beam spot-size. Previous studies reported that silver ions migrate in silver containing materials under influence of electron beam irradiation.⁴⁻¹¹ We have confirmed that the conventional SEM imaging mode (scanning mode) results in randomly located growth of nodules and wires, we showed that continuous exposure to the electron beam in EDX mode results in formation of high-aspect ratio nanorods with controlled dimensions and orientations at the chosen location. Nanoscale manipulation of atoms is desirable for many modern technologies and the results open up a number of exciting possibilities for nanoscale controlled in situ fabrication of nanoparticles and nanowires.

Previous attempts have successfully demonstrated growth of nanowires at random locations within the area irradiated by electron beams.^{5-7, 9, 10, 12, 13} Mesoporous zeolites show high sensitivity to electron beam irradiation under high vacuum and the formation of silver nanorods with high aspect ratios of up to 3000 have been reported in studies on silver containing zeolites,^{6, 7, 10, 14} while copper containing materials can also form high aspect ratio nanorods.¹³ In addition to solid phase transitions, the effect has also been reported in the liquid phase, using Transmission Electron Microscopy (TEM), Scanning Transmission Electron Microscopy (STEM) and Scanning Electron Microscopy (SEM) techniques.^{8, 15-17} For example, silver nanocrystals have been grown from dilute solutions of silver nitrate by STEM irradiation.¹⁸ Fine experimental control over the initiation and the growth process is required for practical applications of the technique for fabrication of designer nanostructures for nano-electronic and nanophotonic applications.

We have demonstrated electron-beam assisted growth of stereoscopic structures with control over nanorod diameter, length and orientation and nanoscale precision in their position on the example of a nanorod-on-nanopillar geometry using as “a substrate” prefabricated silver nanopillars with typical dimensions of 100-250 nm diameter and 1-4 μm length. Hereafter, we refer to structures formed by electron beam as nanorods and the prefabricated base as nanopillars. The nanopillars were formed via electromigration in a thin strip of porous silver. Initially, the porous silver was created by sintering a paste (NanoTach® X Silver paste from NBE Tech) containing silver nanoparticles with an average diameter of 30 nm at 300 °C in air. After sintering, nanorods were formed in the silver stripe by connecting the ends of the stripe to a voltage source (outputting ~ 7 mV across the stripe) to generate a current density of 2.4×10^8 A/m²

for a time period of 240 hours. The electromigration process leads to substrate nanopillars forming all over the surface of the silver stripe as described in detail elsewhere.¹⁹

Methods

The electron beam irradiation experiments were carried out with two different field emission guns (FEGs) in a Hitachi S4000 SEM (FEG-1) and FEI Quanta SEM (FEG-2), both equipped with energy dispersive X-ray (EDX) analysis instruments. FEG-1 was used in the spot mode (EDX regime) to generate nanorods at specific sites and provides an electron beam diameter of 30 nm, accelerating voltage 25 kV, spot diameter 14 nm, beam drift of 5 nm/s, and surface exposure times 10-100 s. The EDX spot mode, concentrating the beam on a point on the surface of a substrate nanopillar was found to result in the formation of individual nanorods at the targeted point of the surface. FEG-2 provides an electron beam diameter of 50 nm, accelerating voltage 25 kV, and spot diameter 20 nm and was used in the scanning mode, with beam drift of 10 nm/s, and surface exposure times of 30-70 s. The normal SEM scanning mode shows that after 2 minutes uninterrupted electron beam scanning, nanoparticles were generated at random locations, covering approximately 5% of the nanopillars. All samples were connected to the SEM stage but the charging was still observed across the sample and in the targeted nanopillar samples in high magnification SEM images. Charging of samples provides a drift velocity of 10 nm/s with FEG-2 and 5 nm/s with FEG-1, which results in the directional formation of nanorods along the drift direction. By changing the orientation of the surface, it is possible to change the direction of drift and, thus, the direction of nanorod formation.

The electron beam of the field-emission gun (FEG-1) was positioned sequentially at multiple points on the Ag surface with a resolution of approximately 5 nm, provided by the

SEM. One can initially observe the formation of the nanoparticles at the position of the electron beam (25 kV for 70 s) which, with the increase of the exposure time, develop into distinct nanorods with increasing aspect ratio. The experiments show that the nanorod diameter can be increased by rescanning the base of an existing nanorod. Since the generated nanorods follow the electron beam drift, the length of nanorods can simply be controlled by changing the exposure time.

Results

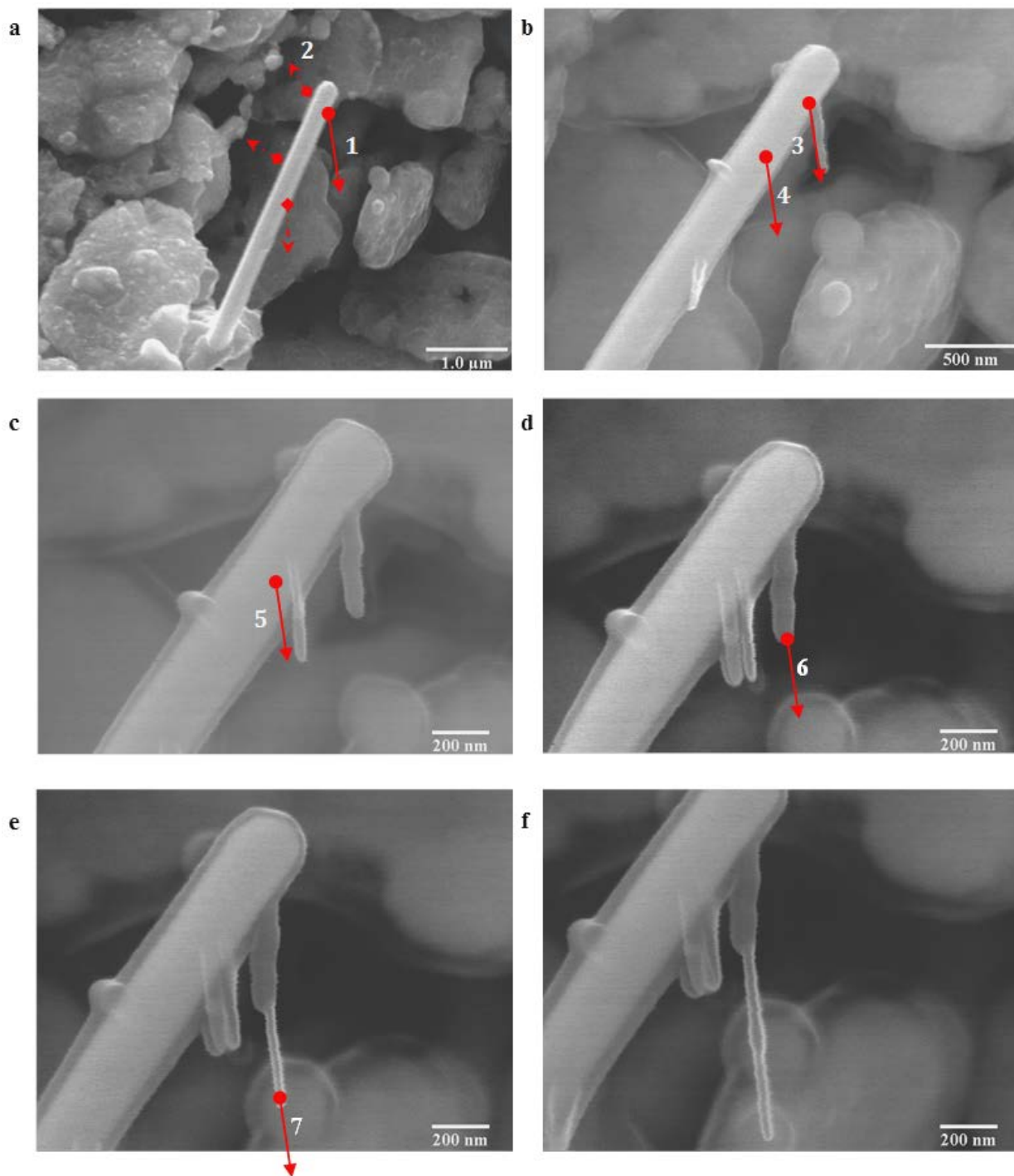


Figure 1. Nanorod growth with precise control over base location, growth direction and size. (a) SEM image of the nanopillar (280 nm diameter and 3.4 μm length) used as a substrate for electron-beam induced growth. Positions of the electron beam and its drift direction are shown

for 4 initial experiments. (b) SEM images of the resulting nanorods and nodules. Positions 3 and 4 of the beam for growing additional nanorods are also shown. (c) SEM image of nanorods after the previous growth cycles. Position 5 of the beam shown for growing an additional nanorod at a distance of 10 nm parallel to nanorod 4. (d) SEM image of the resulting nanorod and the location and displacement of a further beam spot. (e) SEM image of resulting 31 nm diameter nanorod on nanorod structure and location for further nanorod growth. (f) SEM image of the final structure. The growth is performed with the FEG-1 electron beam parameters.

Fig. 1a-f shows the electron-beam spot location and the displacement vector for a number of growth cycles resulting in the formation of nanorods leading to the controllable stereoscopic decoration of the supporting nanopillar. The solid arrows indicate exact displacement vectors calculated from images taken before and after the electron beam irradiation, with the base of the arrow representing the initial location of the e-beam spot. In all cases, except the irradiation event labelled “2”, the exposure time was 70 s but for “2” the time was halved (35 s). The drift direction was altered (Fig. 1a) by changing the orientation of the sample (leaving the tilt unchanged), while the drift velocity was kept at 5 nm/s. Fig. 1b shows the location of two more beam spots and drift directions. The event labelled “3” resulted in a doubling of the thickness of the nanorod grown during the exposure “3” while the event labelled “4” resulted in a new nanorod (Fig. 1c). A further irradiation event labelled “5” results in a new nanorod parallel to the neighbouring nanorod and with the same length at a separation distance of 10 nm (Fig. 1d). The lengths of the nanorods are the same at 340 ± 5 nm. The images in Figs. 1(c) and (d) confirm that at 5 nm/s beam speed, the nanorod growth direction and length can be controlled by the drift during irradiation. Fig. 1d demonstrates that nanorods can be generated parallel to each other with high precision (position control better than 5 nm). They can be grown either parallel to each

other on the substrate (Fig. 1b and c) or indeed on the tips of existing nanorods (Fig. 1d-f). The 34 nm diameter and 375 nm long nanorod in Fig. 1e formed in similar fashion and again 376 nm long nanorod formed on the previously formed nanorods in Fig. 1f. The formed nanorods in Fig. 1e and f consists of both 70 and 32 nm diameter segments, controlled by single and double exposures.

Table 1. Length and diameter of different nanorod formed via Electron Beam Irradiation (EBI) in Figure 1a-f.

Nanorod in Figure 1a-f	Arrow Number 1 (Fig. 1a,b)	Arrow Number 3 (Fig. 1b,c)	Arrow Number 4 (Fig. 1b,c)	Arrow Number 5 (Fig. 1c,d)	Arrow Number 6 (Fig. 1d,e)	Arrow Number 7 (Fig. 1e,f)
Length (nm)	379	375	372	378	375	376
Diameter (nm)	37	70	34	55	34	32

Table 1 lists the nanorods in Fig. 1 and their lengths and widths. While the length of nanorods are controlled by the exposure time, the width exhibits more variability in that while the majority of the widths are 35 ± 5 nm except nanorod 3 which had a double exposure, we see that nanorod 5 has an anomalously large width of 55 nm possibly caused by close proximity to nanorod 4.

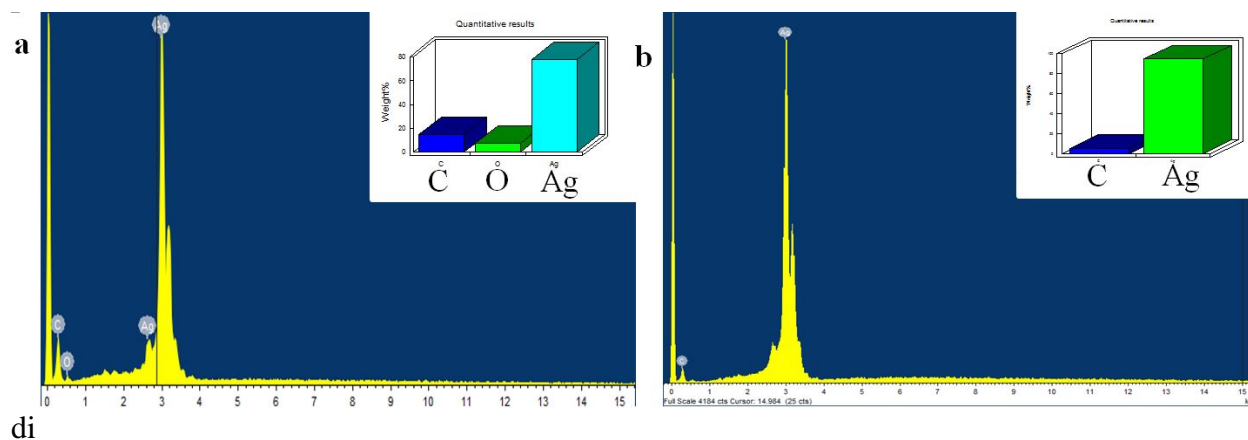


Figure 2. EDX spectra and composition of (a) nanopillar (b) electron-beam-grown nanorod after 70 s EDX irradiation of nanopillar.

The SEM images from nanopillars at high magnification (80000X, Fig. 1c-f) seem to indicate that the nanopillar is covered with a thin 20 nm shell. The core/shell appearance of nanopillars and nanorods at high magnification could indicate the presence of an oxide layer or carbon contamination. The results for energy dispersed X-ray (EDX) spectra are shown in Fig. 2a and b for a particular nanopillar and nanorod but the results are generally true for all nanopillars and nanorods that have been observed. Fig. 2a shows that the nanopillar composition is silver (77.8%), carbon (14.6%) and oxygen (7.6%), while the composition of the generated nanorod (Fig. 2b) is Ag (97%) and carbon (3%). The presence of both carbon and a thin oxide layer are normal on silver surfaces but there is also a possibility that the halo effect is caused by SEM optics at high magnification which is known to result in differing contrast and blurring at the edges of 1D and 2D structures.

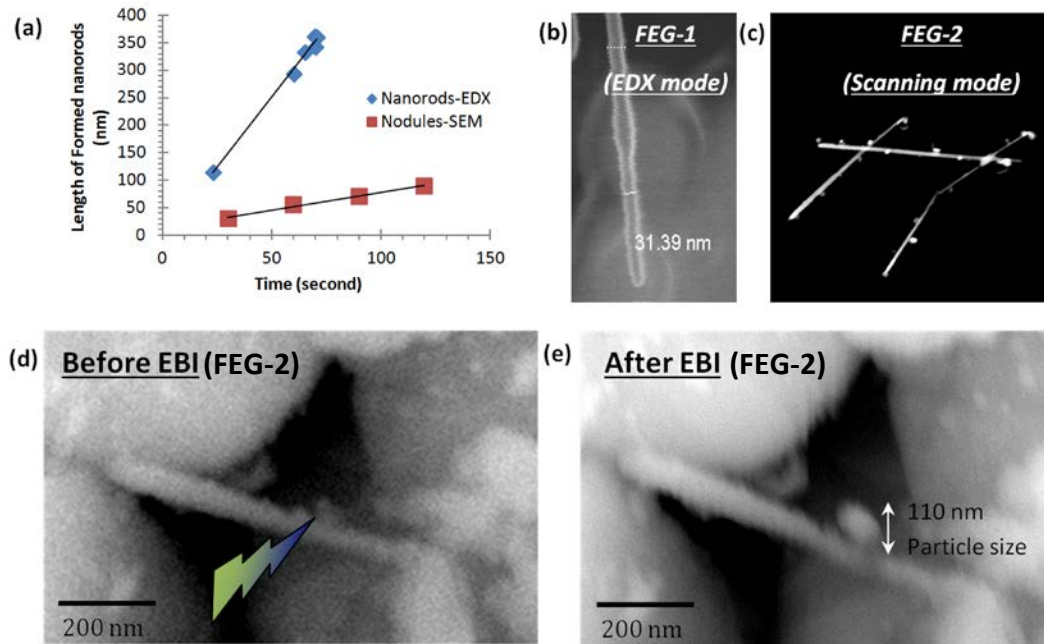


Figure 3. (a) Comparison of the growth rate between nanorods and nodules formed using EDX and SEM respectively; (b) details of nanorod size measurement for growth rate curve; (c) nodules for size measurement for growth rate curve. (d) SEM image with arrow showing EDX spot location before irradiation on a single nanorod (e) SEM image after EDX spot irradiation showing growth of single 110 nm nodule.

Fig. 3a shows that the growth rate as a function of exposure time for nanorods (Fig. 3b) and nodules (Fig. 3c) is higher in spot mode (FEG-1) compared to scanning mode (FEG-2) as expected given the different effective exposure times of the surface to the electron beam. In scanning mode (FEG-2, 25 kV accelerating voltage, Fig. 3c), with the electron beam constantly scanning the surface, low aspect ratio particles are formed after irradiation for 120 s. The size of the nodules approximately doubles from 80 nm to 170 nm, when the electron beam exposure time was doubled from 60 to 120 s. For FEG-2 in EDX spot mode, the drift velocity was double that of the FEG-1 mode and equal to 10 nm/s, resulting in formation of 100 nm nanoparticles at

the spot location (Fig. 3d and e). The Energy Dispersive X-ray (EDX) analysis of the nanoparticles shows the same composition as the nanorods with 97% Ag and 3% carbon. For both FEG-1 and FEG-2 spot-mode experiments the monotonic drift was caused by sample charging. It is proposed that in future, elimination of this constant drift, and creation of a dynamically controlled drift be implemented by using motorized sample stage controls. In the current implementation the drift speed and direction were both constant. The drift at 5 nm/s resulted in growth of high aspect ratio nanorods while the drift at 10 nm/s resulted in growth of nodules. This suggests that the ion drift speed responsible for growth lies between these two values.

Discussion

To the best of our knowledge and as also stated in other studies,⁴⁻⁶ there is no general and comprehensive model explaining the growth mechanism of whiskers and nanostructures due to electron beam irradiation.⁵ In general, the electron beam used in scanning electron microscopy can cause a temporary or permanent change in the surface or bulk structure of a specimen, arising from elastic and inelastic electron scattering and related heating, electrostatic charging, ionization damage (radiolysis), displacement damage, and sputtering. Studies which explicitly result in growth of silver nanostructures under irradiation include.^{4-11, 14} Of these, ref.⁵ appears to be the most relevant as the mechanisms proposed; i) migration of silver ions from a silver nanowire substrate in the presence of an electric field, ii) the presence of an oxide layer (in that publication TiO_2 , in the present work, silver oxide), and iii) stresses caused by thermal gradients caused by electron beam heating are present also in the current work. In general terms, initial heating of the substrate during the interaction with the beam, provides energy for atomic

migration.^{5, 6} This can be also coupled to softening of the internal material structure under the electron irradiation. Charging of the silver under the irradiation simultaneously results in attraction of silver ions to the regions exposed to the electron beam. Additional driving forces are also present due to temperature gradients over the silver surface, which, combined with the electric fields,^{6, 16} continuously drive ions towards the region exposed to the electron beam as it drifts. Longer exposure to the electron beam tends to result in longer, curved whiskers⁵⁻⁷ as opposed to the straight nanorods observed with short exposures.

Conclusions

In summary, electron-beam irradiation has been used to fabricate stereoscopic nanorods on curved surfaces over existing nanoscale structures. Both high control over nanorod dimensions and high placement accuracy have been demonstrated. The conventional SEM imaging mode results in growth of nodules, while continuous exposure to higher energy electron beams, typical of EDX mode results in formation of high aspect ratio nanorods. The nanorod growth rate and direction can be controlled by movement of the electron beam spot over the surface of the substrate at low drift velocities (5 nm/s), caused by charging and could in future be reproduced by manipulation of the SEM stage. The location of the growing nanorods can be controlled by the position of the electron beam spot and can be used to induce growth of nanorods on selected pre-existing nanorods. The method opens up a number of exciting possibilities involving controlled, direct fabrication and manipulation of nanowires in an electron beam using normal SEM facilities. Examples could be the creation of closely spaced parallel structures as has been demonstrated or fabrication of complex three-dimensional plasmonic structures and their networks for applications in sensing, surface enhanced Raman scattering and

photo-chemistry applications. Given the sequential nature of fabrication the first applications would necessarily be small scale lab based applications to produce bespoke 3-d structures made of linear segments branching off at desired angles. Further applications are expected to follow once the properties and unique benefits of these structures are explored.

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Author Contributions

AM performed experiments. All authors were involved with planning the experiments, analysing the results and writing the manuscript.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

TEM, transmission electron microscopy; STEM, Scanning Transmission Electron Microscopy; FIB, focused-ion-beam milling; EBL, electron-beam lithography; FEG-1, filed emission gun 2 on FEI quanta microscope ; FEG-1, filed emission gun 1 on Hitachi S4000 microscope; EBI, electron beam irradiation; SEM, scanning electron microscopy; EDX, Energy Dispersive X-ray;

ACKNOWLEDGMENT

This work was supported, in part, by EPSRC (UK). A.V.Z. acknowledges support from the Royal Society and the Wolfson Foundation. We gratefully acknowledge Messrs G. Vizcay and F. Roland from the Centre for Ultrastructural Imaging (CUI) unit at KCL and W. Luckhurst and Khalid Khatatba from the physics department for their valuable suggestions and help in carrying out the various experimental procedures. The data access statement: all data supporting this research are provided in full in the Results section.

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